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(54) **Surfactants coming from bi- or tri-carboxylic hydroxyacids.**

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(73) Proprietor: **AUSCHEM S.p.A.**
31, Foro Buonaparte
Milan(IT)

(72) Inventor: **Garlisi, Salvatore, Dr.**
32, Via Aosta
I-13100 Vercelli(IT)
Inventor: **Turchini, Luigi**
85, via Archimede
I-20129 Milan(IT)
Inventor: **Albanini, Aurelio, Dr.**
37, via Vigorelli
I-27045 Casteggio Pavia(IT)
Inventor: **Fornara, Dario, Dr.**
34, via Martiri Libertà
I-28020 Massiola Novara(IT)

(74) Representative: **Weinhold, Peter, Dr. et al**
Patentanwälte Dr. V. Schmied-Kowarzik
Dipl.-Ing. G. Dannenberg Dr. P. Weinhold Dr.
D. Gudel Dipl.-Ing. S. Schubert Dr. P. Barz
Siegfriedstrasse 8
W-8000 München 40 (DE)

EP 0 258 814 B1

Description

The present invention relates to surfactants coming from bi- or tri-carboxylic hydroxyacids with polyhydroxylated compounds.

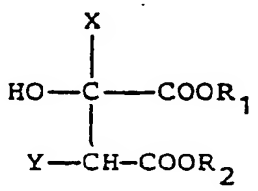
In the great deal of classes of known surfactants it is difficult to find a group of characteristics being all joint in an only product, such as biodegradability, untoxicity, lack of irritant effects on the skin, a high water solubility, in addition to excellent detergent properties, that make such a product particularly versatile and therefore ma ke it utilizable equally for the most different uses such as, for instance, detergency in general, toilette field, beauty culture, foodstuff industry, textile industry, emulsion polymerization and so on.

FR-A-2153449 and FR-A-2153448 disclose builders for detergents and for cleaning products consisting of hydrosoluble salts of esters deriving from di-, tri-, or tetra(hydroxy)carboxylic acids and polyalcohols containing 3 to 6 hydroxy groups or a C_4-C_6 sugar-alcohol.

The products are not surfactants and are useful in detergent compositions as adjuvants owing to their calcium ions sequestring power and their stabilizing effect on the dispersion of the particles of ferric oxide normally present in the aqueous solutions used in washing.

We have now found surfactants coming from bi- or tri-carboxylic hydroxyacids, more particularly consisting of esters of citric, tartaric or malic acid with alkyl ethers of polysaccharides or with hydroxyalkylethers of polyalcohols, as well as of salts thereof with inorganic or organic bases, which surfactants have, in combination, aforesaid good characteristics and therefore proved to be suitable for a great deal of applications.

Therefore the object of the present invention concerns the esters of bi- or tri-carboxylic hydroxy acids having general formula:



(I)

wherein:

X is H or $-CH_2COOR$ group;

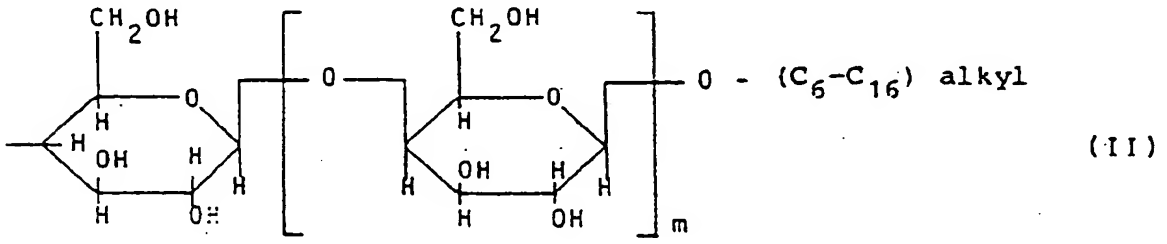
Y is H or -OH, on condition that Y is H when X is $-CH_2COOR$;

R, R_1, R_2, which may be the same or different, represent a hydrogen atom, an alkaline or alkaline-earth metal, an ammonium group, the cation of an ammonium organic base or an A radical coming from a polyhydroxylated organic compound selected from the group comprising etherified (C_6-C_{16}) alkyl polysaccharides containing from 2 to 6 monomeric saccharide units and etherified (C_6-C_{16}) hydroxyalkyl aliphatic polyalcohols containing from 2 to 16 hydroxyl radicals, on condition that at least one of said R, R_1, R_2 is an A radical and wherein hydroxyl radical or hydroxyl radicals of the acid group of the esters having formula (I) may be optionally esterified or etherified by usual methods.

The alkaline metal is selected preferably between sodium and potassium and the alkaline earth metal is preferably magnesium.

The cation of an ammonium organic base may come, for instance, from an alkanolamine such as monoethanolamine or triethanolamine.

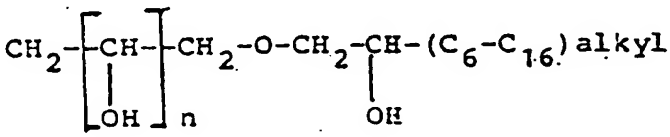
As A radicals coming from etherified (C_6-C_{16}) alkyl polysaccharides, use may be made, for instance, of the ones coming from monoalkyletherified polyglucose having formula:



(II)

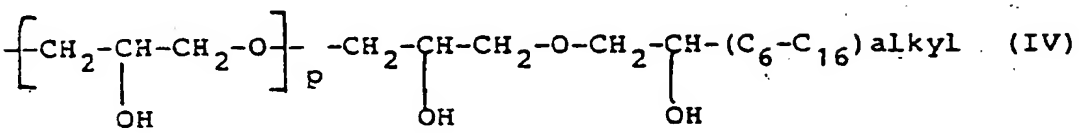
wherein m is a whole number ranging from 1 to 5.

As A radicals, coming from etherified (C_6-C_{16}) hydroxyalkyl aliphatic polyalcohols, use may be made, for instance, of the ones having general formulae:



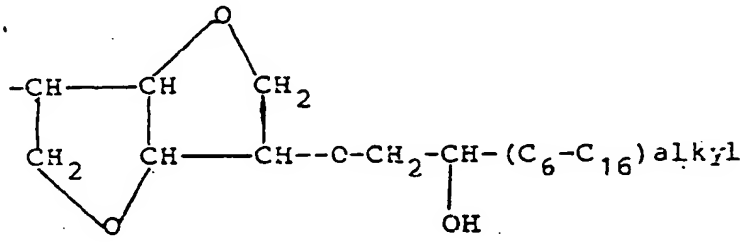
(III)

wherein n is a whole number ranging from 1 to 15;

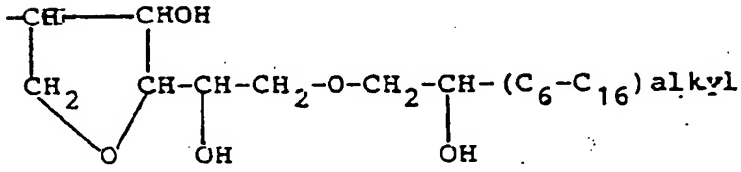


(IV)

wherein p is a whole number ranging from 1 to 10;



(V)



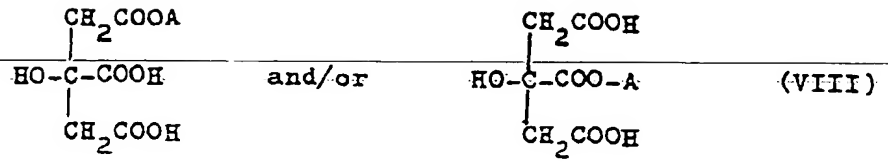
(VI)

The esters having formula (I) are prepared according to a process, and this forms a further object of the present invention, comprising esterification of citric, tartaric or malic acid with a polyhydroxylated organic compound having formula:

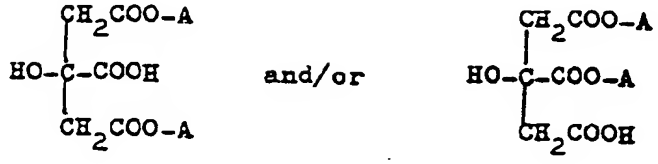
A-OH (VII)

wherein A has aforesaid meaning, by heating at a temperature of 120-140 °C, with continuous distillation of the water forming during the reaction and optional final salification of the obtained product by means of bases of alkaline or alkaline-earth metals, ammonia or amines. As base use may be made, for instance, of sodium, potassium, magnesium, ammonium hydroxide, triethanolamine or monoethanolamine.

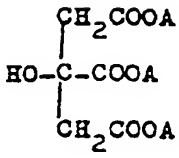
By aforesaid process, starting from citric acid, one obtains mono-di-and triesters having the following formulae respectively:



(VIII)

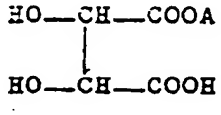


(IX)



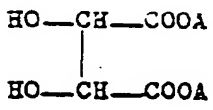
(X)

Starting from tartaric acid one obtains mono-, and di-esters having the following formulae respectively:



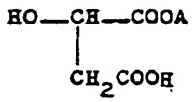
(XI)

and

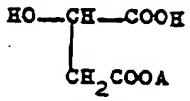


(XII)

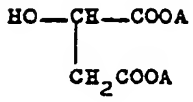
Starting from malic acid one obtains mono- and di-esters having the following formulae respectively:



and/or



(XIII)

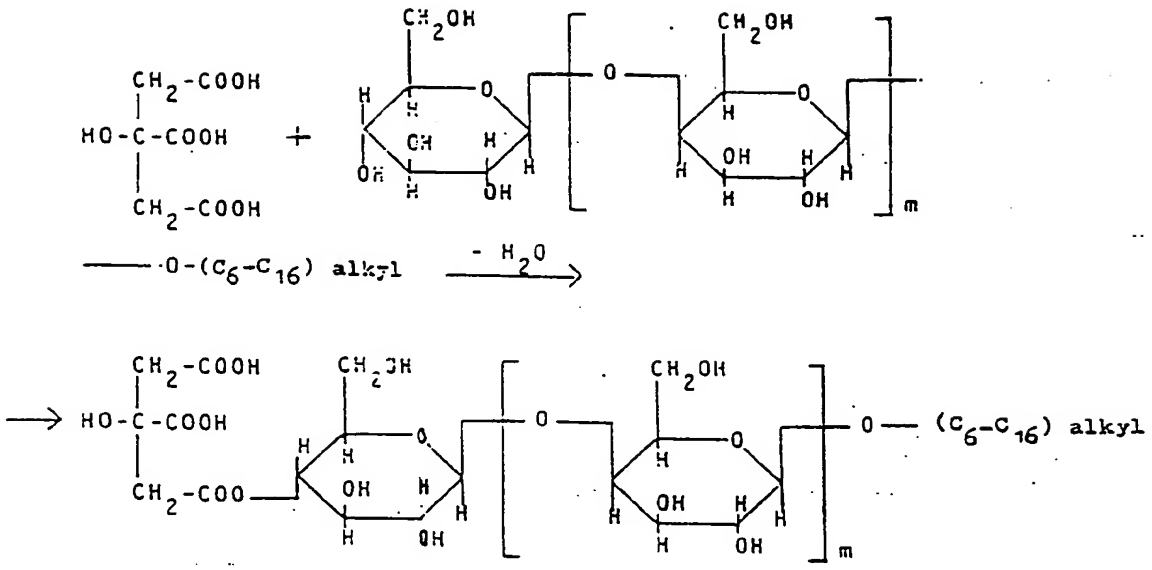


(XIV)

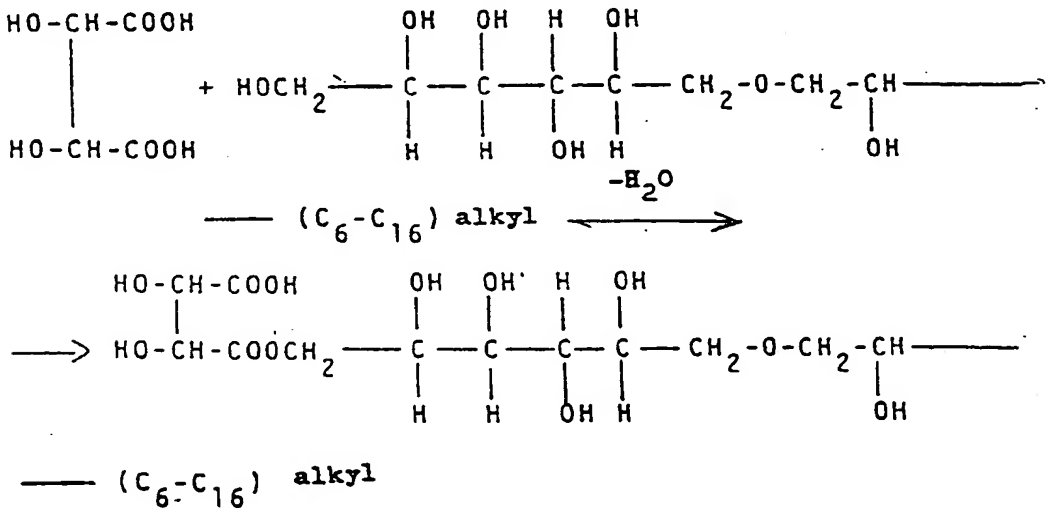
According to the employed reaction conditions and according to the molar ratios hydroxyacid/polyhydroxylated compound it is possible to prepare in preference mono-, di- and in the case of citric acid, triester as well.

Thus hydroxyacid and polyhydroxylated compound (VII) are reacted in substantially equimolecular ratios in order to produce preferably monoesters having formulae (VIII), (XI) and (XIII).

In the case of the preparation of citric monoester of monoalkyletherified polyglucose, the reaction may be carried out according to the following equation:



In the case of the preparation of tartaric monoester of monohydroxyalkyletherified sorbitol, the reaction may be carried out according to the following equation:



The polyhydroxylated organic compounds having formula (VII), such as alkyletherified polysaccharides and hydroxyalkyletherified polyalcohols are known products or may be prepared by known methods and sometimes they may be found on the market.

In particular the monoalkyletherified polysaccharides may be prepared by etherification of the polysaccharide with (C_6-C_{16}) fatty alcohols.

The monohydroxyalkyletherified polyalcohols may be prepared by reaction of the polyalcohol with a (C_6-C_{16}) alkyl α-epoxide.

Among the alkyletherified polysaccharides preference is given to polyglucose monoalkyletherified with octylic and decylic alcohols.

Among the hydroxyalkyletherified polyalcohols preference is given to sorbitol monohydroxyalkyletherified with octene-1-oxide and/or decene-1-oxide.

The esters according to the present invention and in particular the monoesters of alkyletherified polysaccharides or of hydroxyalkyletherified polyalcohols, salts and mixtures thereof are very efficient

surfactants, allowing, even when employed in very low percentages, a remarkable lowering of the surface tension and therefore they may be used as emulsifiers, dispersing agents or detergents in general.

Besides the excellent detergent properties, they do not present any toxic effect, as well as any irritant effect on skin and eyes and they do not present any acute toxicity if they are swallowed orally.

They are highly biodegradable, showing biodegradability values over 90%.

They prove to be stable within a wide range of temperatures up to 100 °C and after a storage at low temperatures for a long time, when they are brought to room temperature, do not give rise to any separation.

They show a good but not excessive wetting power and a good foam forming power. They may have from a moderate to an excellent water solubility.

In particular their solubility increases, by increasing the number of hydroxyl radicals of the polyhydroxylic part of the alkyletherified or hydroxyalkyletherified compound.

The esters, according to the invention, proved to be compatible with most of known surfactants and therefore they may be formularized with them.

The esters, according to the invention, on account of their whole of characteristics, proved to be very flexible as to the different applications of the surface-active agents.

On account of their high detergent power joint to lack of toxic effects on the skin, hair, eyes, the esters are particularly suitable for their applications in the beaty culture field such as, for instance, for the preparation of liquid or creamy detergents for the skin, shampoos, bath foams.

The following examples will illustrate the invention, without limiting, however, its scope.

EXAMPLE 1

Preparation of esters of citric acid by polyglucose monoalkylethers.

Esterification

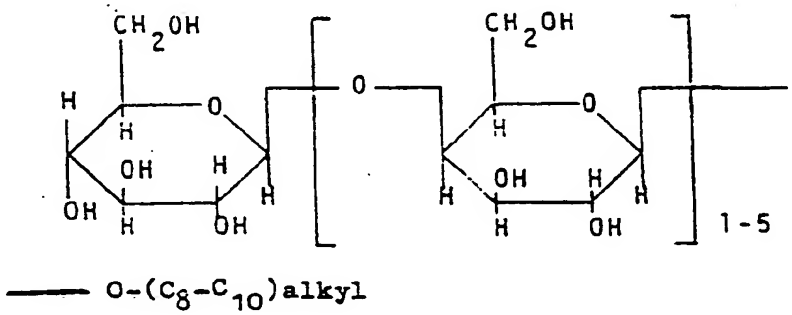
144.0 g (0.75 moles) of anhydrous citric acid and 784.9 g (0.75 moles) of TRITON-CG/110® at 60% in water were fed, under nitrogen flow, into a reactor equipped with a heating system, stirrer, vacuum pipe connection, thermometer, system for feeding the reactants and connected to a cooler equipped with a manifold for collecting the dilution water and successively the reaction water.

Vacuum was produced inside the apparatus, by means of a water pump, and while keeping the mixture under stirring, the temperature was brought to 90°-105°C, in about 40 minutes in order to remove the dilution water, afterwards, vacuum was stopped and the temperature was brought to 124-125°C under nitrogen flow; the reaction mixture was kept at this temperature over about 100 minutes, till acid value was 145± 3.

The mixture was cooled up to a temperature of 110°-115°C, diluted with about 300 g of water, equal to 50% of the calculated amount of acid monoester, cooled up to 50°C and finally the reactor was unloaded.

One obtained 900 g of a limpid liquid product containing 33.33% of water, having an acid value of 97.4 and a saponification number of 140, substantially consisting of citric acid monoester.

TRITON-CG/110® consisted of a mixture of polyglucose monoalkylethers at 60% in water of formula:



having a hydroxyl number of 879.9, determined on the dry product, obtained by etherification of polyglucose containing from 2 to 6 glucose units with a mixture 50/50 of octylic and decylic alcohol.

Salification

339.6 g of the citric monoester at 66.66% in water, prepared before and 581.7 g of demineralized water were fed into a vessel equipped with a stirrer, thermometer, dropping funnel and water cooling system.

The mixture was stirred till a limpid solution was obtained, afterwards, under stirring, 78.7 g of an aqueous solution of NaOH at 30% were fed slowly, in about 1 hour, through a dropping funnel, while keeping the temperature at values below 30 °C.

One obtained 1000 g of a limpid aqueous solution containing 25% by weight of citric monoester salified with sodium.

The solution, thus obtained, could be employed, either as such or after having been diluted, for the different uses of detergency.

An utter viscous limpid liquid was obtained from the solution, after having removed the water by heating at 50 °C over 16 hours under vacuum; such a liquid consisted prevailingly of sodic salt of citric monoester, having an acid value of 5, a saponification number of 71.0, an esterification number of 66.0 and a pH value of 6.8 at 1%.

The salified product proved to be perfectly soluble in water in any ratio, yielding limpid solutions at 25 °C up to a concentration of 25% and more or less viscous solutions at higher concentrations.

Moreover the following tests were carried out on the salified product:

- Surface tension

The surface tension, measured at 20 °C according to DU NOUY method, was 42.0 dynes/cm at a concentration of 0.25 g/l and 32.3 dynes/cm at a concentration of 1 g/l.

- Imbibition power

Imbibition power, determined on the product at a concentration of 2 g/l in distilled water, was over 1800 seconds.

- Foam forming power

It was determined on 200 ml of an aqueous solution containing 2 g/l of the product, by using a bored flat piston system, 50 strokes. The following results were obtained:

After minutes	foam ml
0	790
5	780
10	770
15	770
20	770
25	760
30	760

Moreover the salified product proved to be highly biodegradable, untoxic, unirritant and endowed with an excellent detergent power.

EXAMPLE 2

Preparation of esters of tartaric acid by polyglucose monoalkylethers.

Esterification

75.1 g (0.5 moles) of anhydrous tartaric acid and 523.2 g (0.5 moles) of TRITON-CG/110® at 60% in water were fed, under nitrogen flow, into a reactor equipped with a heating system, stirrer, vacuum pipe connection, thermometer, system for feeding the reactants and connected to a cooler equipped with a manifold for collecting the dilution water and successively the reaction water.

Vacuum was produced inside the apparatus, by means of a water pump, and while keeping the mixture under stirring, the temperature was brought to 90-105 °C in about 50 minutes, in order to remove the dilution water, afterwards, vacuum was stopped and the temperature was brought to 118-120 °C under nitrogen flow; the reaction mixture was kept at this temperature over about 90 minutes, till acid value was 85± 3.

The mixture was cooled up to a temperature of 110-115 °C, diluted with about 188 g of water, equal to 50% of the calculated amount of acid monoester, cooled up to about 50 °C and finally the reactor was unloaded.

One obtained 564 g of a limpid liquid product , containing 33.33% of water, having an acid value of 50.0 and a saponification number of 98.4, substantially consisting of tartaric acid monoester.

Salification

356.1 g of the tartaric monoester at 66.66% in water, prepared before, and 601.5 g of demineralized water were fed into a vessel equipped with a stirrer, thermometer, dropping funnel and water cooling system.

The mixture was stirred till a limpid solution was obtained, afterwards, under stirring 42.4 g of an aqueous solution of NaOH at 30% were fed, slowly in about 1 hour, through a dropping funnel, while keeping the temperature at values below 30 °C.

One obtained 1000 g of a limpid aqueous solution containing 25% by weight of tartaric monoester, salified with sodium.

The solution, thus obtained, could be employed, either as such or after having been diluted, for the different uses of detergency.

An utter viscous limpid liquid was obtained from the solution, after having removed the water by heating at 50 °C over 16 hours, under vacuum; such a liquid consisted prevailingly of sodic salt of tartaric monoester, having an acid value of 2.4, a saponification number of 77.2, an esterification number of 74.8 and a pH value of 6.8 at 1%.

The salified product proved to be perfectly soluble in water in any ratio, yielding limpid solutions at 25 °C up to a concentration of 25% and more or less viscous solutions at higher concentrations.

Moreover the following tests were carried out on the salified product:

- Surface tension

The surface tension, measured at 20 °C, according to DU NOUY method, was 43.5 dynes/cm at a concentration of 0.25 g/l and 30.0 dynes/cm at a concentration of 1 g/l.

- Imbibition power

Imbibition power, determined on the product at a concentration of 2 g/l in distilled water, was over 1800 seconds.

- Foam forming power

It was determined on 200 ml of an aqueous solution containing 2 g of the product, by using a bored flat piston system, 50 strokes. The following results were obtained:

After minutes	foam ml
0	790
5	780
10	780
15	780
20	770
25	770
30	760

Moreover the salified product proved to be highly biodegradable, untoxic, unirritant and endowed with an excellent detergent power.

EXAMPLE 3

Preparation of monoester of citric acid by sorbitol 2-hydroxyoctyl-ether.

Esterification

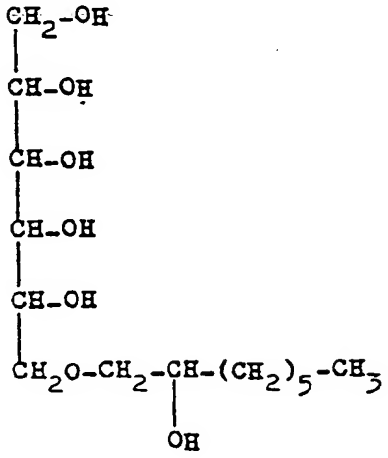
126.7 g (0.66 moles) of anhydrous citric acid and 200.0 g (0.66 moles) of sorbitol 2-hydroxyoctyl-ether were fed, under nitrogen flow, into a reactor equipped with a heating system, stirrer, thermometer, system for feeding the reactants and connected to a cooler equipped with a manifold for collecting the reaction water.

The temperature was brought, under stirring and nitrogen flow, to 140-142 °C in about 90 minutes and the reaction mixture was kept at this temperature for about 50 minutes, till acid value was 240± 5.

The mixture was cooled up to a temperature of 110-115 °C, diluted with about 157 g of water, equal to 50% of the calculated amount of acid monoester, cooled up to 50 °C and finally the reactor was unloaded.

One obtained 471 g of a viscous liquid containing 33.33% of water, having an acid value of 156.8 and a saponification number of 235.2, substantially consisting of citric acid monoester.

Sorbitol 2-hydroxyoctyl-ether having formula:



having a hydroxyl number of 1111.0 and a molar weight of 303, was obtained, by reacting sorbitol with octene-1-oxide.

Salification

321.2 g of the citric monoester at 66.66% in water, prepared before, and 559.2 g of demineralized water were fed into a vessel equipped with a stirrer, thermometer, dropping funnel and water cooling system.

The mixture was stirred till a homogeneous emulsion was obtained, afterwards under stirring, 119.6 g of an aqueous solution of NaOH at 30% were fed slowly in about 1 hour, through a dropping funnel, while keeping the temperature at values below 30 °C.

1000 g of a slightly cloudy aqueous solution were obtained. Then by paper filtration one obtained a limpid aqueous solution containing 25% by weight of citric monoester salified with sodium.

The solution, thus obtained, may be used either as such or after having been diluted, for the different uses of detergency.

An utter viscous limpid liquid was obtained from the solution, after having removed the water by heating at 50 °C over 16 hours under vacuum; such a liquid consisted prevailingly of sodic salt of citric monoester, having an acid value of 4.5, a saponification number of 119.4, an esterification number of 114.9 and a pH value of 6.8 at 1%.

The salified product proved to be perfectly soluble in water in any ratio, yielding limpid solutions at 25 °C up to a concentration of 25% and more or less viscous solutions at higher concentrations.

The following tests were carried out on the salified product:

- Surface tension

The surface tension, measured at 20 °C, according to DU NOUY method, was 29.5 dynes/cm at a concentration of 0.25 g/l and 27.5 dynes/cm at a concentration of 1 g/l.

- Imbibition power

Imbibition power, determined on the product at a concentration of 2 g/l in distilled water was over 1800 seconds.

- Foam forming power

It was determined on 200 ml of an aqueous solution, containing 2 g/l of the product, by using a bored flat piston system, 50 strokes. The following results were obtained:

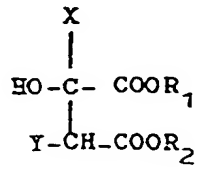
After minutes	foam ml
0	530
5	530
10	520
15	510
20	480
25	450
30	410

Moreover the salified product proved to be highly biodegradable, untoxic, unirritant and endowed with an excellent detergent power.

Claims

Claims for the following Contracting States : BE, CH, DE, FR, GB, LI, NL

1. Esters of bi- or tri-carboxylic hydroxyacids having general formula:



(I)

wherein:
X is H or $-CH_2COOR$ group;
Y is H or -OH, on condition that Y is H when X is $-CH_2COOR$;
R, R_1, R_2, which may be the same or different, represent a hydrogen atom, an alkaline or alkaline-earth metal, an ammonium group, the cation of an ammonium organic base or an A radical coming from a polyhydroxylated organic compound selected from the group comprising etherified (C_6-C_{16}) alkyl polysaccharides containing from 2 to 6 monomeric saccharide units and etherified (C_6-C_{16}) hydroxyalkyl aliphatic polyalcohols containing from 2 to 16 hydroxyl radicals, on condition that, at least one of said R, R_1, R_2, is an A radical.

2. Esters, according to claim 1, wherein A radical is selected from the group comprising polyglucose (C_6-C_{16}) monoalkyl ethers, containing from 2 to 6 glucose units, and sorbitol (C_6-C_{16}) monohydroxyalkyl ethers.

3. Esters according to one or both of the claims 1-2, wherein the hydroxyl radical or the hydroxyl radicals of the acid group of the esters having formula (I) are esterified or etherified by usual methods.

4. Esters according to claim 1, namely citric acid monoesters, with polyglucose (C_8-C_{10}) monoalkylethers containing from 2 to 6 glucose units and salts thereof with inorganic or organic bases, respectively, or with sorbitol 2-hydroxyoctylether and salts thereof with inorganic or organic bases, respectively.

5. Esters according to claim 1, namely tartaric acid monoesters, with polyglucose (C_8-C_{10}) monoalkyl ethers, containing from 2 to 6 glucose units and salts thereof with inorganic or organic bases, respectively, or with sorbitol 2-hydroxy octylether and salts thereof with inorganic or organic bases, respectively.

6. A process for preparing the esters having formula (I) according to claim 1, consisting in esterifying citric, tartaric or malic acid with a polyhydroxylated compound having formula:

A-OH (VIII)

wherein A has the meaning according to claim 1, by heating at a temperature of 120-140°C, with continuous distillation of the water forming during the reaction and optional salification of the obtained product, with bases of alkaline or alkaline-earth metals, ammonia or amines.

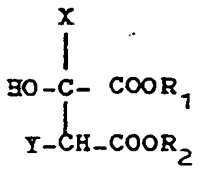
7. A process according to claim 6, wherein A radical is selected from the group comprising polyglucose (C_6-C_{16}) monoalkyl ethers containing from 2 to 6 glucose units and sorbitol (C_6-C_{16}) monohydroxyalkyl ethers.

8. Cosmetic and detergent compositions containing one or more esters according to one or more of the claims form 1 to 5.

9. Use of the esters according to one or more of the claims 1-5, as surface-active agents.

Claims for the following Contracting State : ES

1. A process for preparing the esters of bi- or tricarboxylic hydroxyacids having general formula:



(I)

wherein:
X is H or $-CH_2COOR$ group;
Y is H or -OH, on condition that Y is H when X is $-CH_2COOR$;
R, R_1, R_2, which may be the same or different, represent a hydrogen atom, an alkaline or alkaline-earth metal, an ammonium group, the cation of an ammonium organic base or an A radical coming from a polyhydroxylated organic compound selected from the group comprising etherified (C_6-C_{16}) alkyl polysaccharides containing from 2 to 6 monomeric saccharide units and etherified (C_6-C_{16}) hydroxyalkyl aliphatic polyalcohols containing from 2 to 16 hydroxyl radicals, on condition that, at least one of said R, R_1 R_2, is an A radical.
this process consists in esterifying citric, tartaric or malic acid with a polyhydroxylated compound having formula:

A-OH (VIII)

wherein A has the meaning according to claim 1, by heating at a temperature of 120-140°C, with continuous distillation of the water forming during the reaction and optional salification of the obtained product, with bases of alkaline or alkaline-earth metals, ammonia or amines.

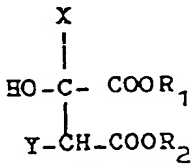
2. A process according to claim 1, wherein A radical is selected from the group comprising polyglucose (C_6-C_{16}) monoalkyl ethers containing from 2 to 6 glucose units and sorbitol (C_6-C_{16}) monohydroxyalkyl ethers.

3. Cosmetic and detergent compositions containing one or more esters obtained by the process according to at least one of the claims 1 to 2.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, CH, DE, FR, GB, LI, NL

1. Ester von Hydroxy-substituierten Bi- oder Tricarbonsäuren mit der allgemeinen Formel :



(I)

in der:

X H oder eine $-CH_2COOR$-Gruppe ist;

Y H oder -OH ist, unter der Bedingung, daß Y H ist, wenn X $-CH_2COOR$ ist;

R, R_1, R_2, die gleich oder verschieden sein können, ein Wasserstoffatom, ein Alkali- oder Erdalkalimetall, eine Ammoniumgruppe, das Kation einer ammoniumorganischen Base oder einen A-Rest, der von einer polyhydroxylierten organischen Verbindung stammt, die aus der Gruppe, die veretherte (C_6-C_{16})-Alkyl-Polysaccharide mit 2 bis 6 monomeren Saccharideinheiten und veretherte aliphatische (C_6-C_{16})-Hydroxyalkyl-Polyole mit 2 bis 16 Hydroxylresten umfaßt, ausgewählt ist, bedeuten, unter der Bedingung, daß mindestens eine der Gruppen R, R_1, R_2 ein A-Rest ist.

2. Ester nach Anspruch 1, worin der A-Rest ausgewählt ist aus der Gruppe, die Polyglukose-(C_6-C_{16})-monoalkylether mit 2 bis 6 Glukoseeinheiten und Sorbit-(C_6-C_{16})-Monohydroxyalkylether umfaßt.

3. Ester nach einem oder beiden der Ansprüche 1 - 2, worin der Hydroxylrest oder die Hydroxylreste der Säuregruppe des Esters der Formel (I) nach den üblichen Methoden verestert oder verethert ist (sind).

4. Ester nach Anspruch 1, nämlich Zitronensäuremonoester, mit Polyglukose-(C_8-C_{10})-monoalkylethern mit 2 bis 6 Glukoseeinheiten und Salze derselben mit anorganischen bzw. organischen Basen oder mit Sorbit-2-hydroxyoctylether und Salze desselben mit anorganischen bzw. organischen Basen.

5. Ester nach Anspruch 1, nämlich Weinsäuremonoester mit Polyglukose-(C_8-C_{10})-monoalkylethern mit 2 bis 6 Glukoseeinheiten und Salze derselben mit anorganischen bzw. organischen Basen oder mit Sorbit-2-hydroxyoctylether und Salze desselben mit anorganischen bzw. organischen Basen.

6. Verfahren zur Herstellung der Ester der Formel (I) gemäß Anspruch 1, bestehend aus der Veresterung von Zitronen-, Wein- oder Äpfelsäure mit polyhydroxylierten Verbindungen der Formel:

A-OH (VIII)

worin A die in Anspruch 1 genannte Bedeutung hat, durch Erhitzen auf eine Temperatur von 120 bis 140 °C unter kontinuierlichem Abdestillieren des während der Reaktion gebildeten Wassers und gegebenenfalls Salzbildung des erhaltenen Produkts mit Basen von Alkali- oder Erdalkalimetallen, Ammoniak oder Aminen.

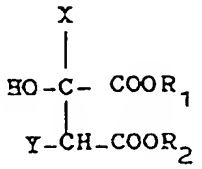
7. Verfahren nach Anspruch 6, worin der A-Rest ausgewählt ist aus der Gruppe, die Polyglukose-(C_6-C_{16})-monoalkylether mit 2 bis 6 Glukoseeinheiten und Sorbit-(C_6-C_{16})-monohydroxyalkylether umfaßt.

8. Kosmetische und Waschmittelzusammensetzungen, die einen oder mehrere der Ester nach einem oder mehreren der Ansprüche 1 bis 5 enthalten.

9. Verwendung der Ester gemäß einem oder mehreren der Ansprüche 1 bis 5 als oberflächenaktive Mittel.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung von Estern von Hydroxy-substituierten Bi- oder Tricarbonsäuren mit der allgemeinen Formel:



(I)

in der:

X H oder eine $-CH_2COOR$-Gruppe ist;

Y H oder -OH ist, unter der Bedingung, daß Y H ist, wenn X $-CH_2COOR$ ist;

R, R_1, R_2, die gleich oder verschieden sein können, ein Wasserstoffatom, ein Alkali- oder Erdalkalimetall, eine Ammoniumgruppe, das Kation einer ammoniumorganischen Base oder einen A-Rest, der von einer polyhydroxylierten organischen Verbindung stammt, die aus der Gruppe, die veretherte (C_6-C_{16})-Alkyl-Polysaccharide mit 2 bis 6 monomeren Saccharideinheiten und veretherte aliphatische (C_6-C_{16})-Hydroxyalkyl-Polyole mit 2 bis 16 Hydroxylresten umfaßt, ausgewählt ist, bedeuten, unter der Bedingung, daß mindestens eine der Gruppen R, R_1, R_2 ein A-Rest ist,
wobei das Verfahren im Verestern von Zitronensäure, Wein- oder Äpfelsäure besteht mit einer polyhydroxylierten Verbindung der Formel:

A-OH (VIII)

worin A die in Anspruch 1 genannte Bedeutung hat, durch Erhitzen auf eine Temperatur von 120 bis 140 °C unter kontinuierlichem Abdestillieren des während der Reaktion gebildeten Wassers und gegebenenfalls Salzbildung des erhaltenen Produkts mit Basen von Alkali- oder Erdalkalimetallen, Ammoniak oder Aminen.

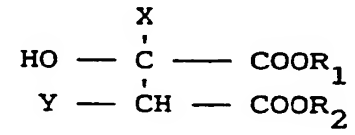
2. Verfahren nach Anspruch 1, worin der A-Rest ausgewählt ist aus der Gruppe, die Polyglukose-(C_6-C_{16})-monoalkylether mit 2 bis 6 Glukoseeinheiten und Sorbit-(C_6-C_{16})-Monohydroxyalkylether umfaßt.

3. Kosmetische und Waschmittelzusammensetzungen, die einen oder mehrere der Ester, erhalten durch das Verfahren nach mindestens einem der Ansprüche 1 und 2, enthalten.

Revendications

Revendications pour les Etats contractants suivants : BE, CH, DE, FR, GB, LI, NL

1. Esters d'hydroxyacides bi- ou tricarboxyliques ayant la formule générale:



(I)

dans laquelle:

X est H ou un groupe $-CH_2COOR$;

Y est H ou -OH, du moment que Y est H quand X est $-CH_2COOR$;

R, R_1 et R_2, qui peuvent être identiques ou différents, représentent chacun un atome d'hydrogène, un métal alcalin ou alcalino-terreux, un groupe ammonium, le cation d'une base organique à base d'ammonium ou un radical A dérivant d'un composé organique polyhydroxylé choisi parmi l'ensemble comprenant les (alkyles en C_6 à C_{16})-polysaccharides éthérifiés, contenant de 2 à 6 motifs saccharides monomères et

des polyalcools (hydroxyalkyles en C_6 à C_{16})-aliphatiques éthérifiés contenant de 2 à 16 radicaux hydroxyles, du moment qu'au moins l'un desdits radicaux R, R_1, R_2 est un radical A.

2. Esters, selon la revendication 1, dans lesquels le radical A est choisi parmi l'ensemble comprenant les éthers monoalkyliques en C_6-C_{16} du polyglucose, contenant de 2 à 6 motifs glucose, et les éthers monohydroxyalkyliques en C_6-C_{16} du sorbitol.

3. Esters selon l'une des revendications 1 et 2, ou selon les deux, dans lesquels le radical hydroxyle ou les radicaux hydroxyles du groupe acide des esters de formule 1 sont estérifiés ou éthérifiés par des procédés usuels.

4. Esters selon la revendication 1, plus précisément monoesters de l'acide citrique, avec des éthers monoalkyliques en C_8-C_{10} du polyglucose contenant de 2 à 6 motifs glucose, et leurs sels respectivement avec des bases minérales ou organiques, ou encore avec l'éther 2-hydroxyoctylique du sorbitol et ses sels respectivement avec des bases minérales ou organiques.

5. Esters selon la revendication 1, plus précisément esters de l'acide monotartrique, avec des éthers monoalkyliques en C_8-C_{10} du polyglucose contenant de 2 à 6 motifs glucose, et leurs sels avec respectivement des bases minérales ou organiques, ou avec l'éther 2-hydroxyoctylique du sorbitol respectivement avec des bases organiques ou minérales.

6. Procédé pour préparer les esters de formule (I) selon la revendication 1, qui consiste à estérifier l'acide citrique, l'acide tartrique ou l'acide malique avec un composé hydroxylé de formule:

A-OH (VIII)

dans laquelle A a les significations données dans la revendication 1, par chauffage à une température de 120 à 140 °C sous distillation continue de l'eau qui se forme pendant la réaction, et éventuellement salification du produit obtenu, avec des bases de métaux alcalins ou alcalino-terreux, l'ammoniac ou des amines.

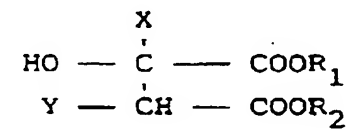
7. Procédé selon la revendication 6, dans lequel le radical A est choisi parmi l'ensemble comprenant les éthers monoalkyliques en C_6-C_{16} du polyglucose contenant de 2 à 6 motifs glucose, et des éthers monohydroxyalkyliques en C_6-C_{16} du sorbitol.

8. Compositions cosmétiques et détergentes contenant un ou plusieurs esters selon une ou plusieurs des revendications 1 à 5.

9. Utilisation des esters selon une ou plusieurs des revendications 1 à 5 en tant qu'agents tensio-actifs.

Revendications pour l'Etat contractant suivant : ES

1. Procédé de préparation d'esters d'hydroxyacides bi-ou tricarboxyliques ayant la formule générale:



(I)

dans laquelle:

X est H ou un groupe $-CH_2COOR$;

Y est H ou -OH, du moment que Y est H quand X est $-CH_2COOR$;

R, R_1 et R_2, qui peuvent être identiques ou différents, représentent chacun un atone d'hydrogène, un métal alcalin ou alcalino-terreux, un groupe ammonium, le cation d'une base organique à base d'ammonium ou un radical A dérivant d'un composé organique

polyhydroxylé choisi parmi l'ensemble comprenant les (alkyles en C_6 à C_{16})-polysaccharides éthérifiés, contenant de 2 à 6 motifs saccharides monomères et des polyalcools (hydroxyalkyles en C_6 à C_{16})-aliphatiques éthérifiés contenant de 2 à 16 radicaux hydroxyles, du moment qu'au moins l'un desdits radicaux R, R_1, R_2 est un radical A,

ledit procédé consistant à estérifier l'acide citrique, l'acide tartrique ou l'acide malique avec un composé hydroxylé de formule:

A-OH (VIII)

dans laquelle A a les significations données dans la revendication 1, par chauffage à une température de 120 à 140 °C sous distillation continue de l'eau qui se forme pendant la réaction, et éventuellement salification du produit obtenu, avec des bases de métaux alcalins ou alcalino-terreux, l'ammoniac ou des amines.

2. Procédé selon la revendication 1, dans lequel le radical A est choisi parmi l'ensemble comprenant les éthers monoalkyliques en C_6-C_{16} du polyglucose contenant de 2 à 6 motifs glucose, et des éthers monohydroxyalkyliques en C_6-C_{16} du sorbitol.

3. Compositions cosmétiques et détergentes contenant un ou plusieurs esters obtenu(s) par le procédé selon la revendication 1 à 2.